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Osmium isotopes in hydrothermal fluids from the Juan de Fuca Ridge

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Abstract

We present Os data for axial high-temperature and off-axial low-temperature hydrothermal solutions from the Juan de Fuca Ridge. The high-temperature, H_2S-bearing axial fluids have unradiogenic Os isotopes pointing to a nearly complete domination of osmium isotopes from the basalts during hydrothermal circulation. The ridge axis fluids typically do not show large enrichment in osmium concentration over seawater although one high-temperature fluid has an Os concentration enhanced by a factor of 4 above seawater. It appears that the Os concentration of high-temperature hydrothermal fluids is typically buffered at roughly the seawater concentration. We suggest that subseafloor precipitation of pyrite from the high-temperature hydrothermal fluids controls the osmium transportation. The axial hydrothermal activity does not supply significant amounts of unradiogenic osmium to the deep oceans. In contrast, a low-temperature off-axis fluid is enriched in non-radiogenic osmium over seawater by a factor of 9, showing much less precipitation of osmium at low temperature. Because a large fraction of the cooling of oceanic lithosphere occurs on ridge flanks, Os from low-temperature, ridge-flank hydrothermal circulation may be a significant contributor to the balance of Os in the oceans. A detailed balance between Os contributions from dissolution of cosmic dust and hydrothermal fluids is still not possible. The low-temperature hydrothermal sample gives $^{187}Os/^{188}Os = 0.110 \pm 0.001$. This extremely unradiogenic osmium can only come from a source that underwent depletion of Re over 2.6 Ga ago. Assuming no contamination during sample collection, this result suggests that the convecting upper mantle contains ancient depleted material that imparted unradiogenic osmium to intruding basaltic melts.

Keywords: osmium; Juan de Fuca Ridge; hydrothermal conditions; isotope ratios

1. Introduction

We present the first data for osmium concentrations and isotopic compositions of hydrothermal fluids and provide an estimate of the flow rate of osmium into the oceans leached from the oceanic crust. It is generally believed that the osmium

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budget of the oceans is governed by inputs from the continents (rivers and aerosols), extraterrestrial matter (cosmic dust/micrometeorites) and from the oceanic crust (hydrothermal fluids and submarine alteration) [1]. On average, $^{187}Os/^{188}Os$ of cosmic material and oceanic crust (=mid-ocean ridge basalt, MORB) are nearly identical ($\sim$0.125) and about ten times lower than that of continental matter ($\sim$1.26) (e.g. [2]). About 4/5th of osmium currently dissolved in the oceans ($^{187}Os/^{188}Os = 1.06$) is of continental derivation [1,3]. However, a quantitative assessment of the relative contributions of oceanic crust and cosmic sources has not been possible because of the absence of data for hydrothermal fluids and the uncertainty in the total cosmic dust infall and the fraction that is dissolved in the oceans. Indeed, while assignments of significant cosmic dust infall are required by the data on deep-sea sediments, calculations suggest that almost all of the remaining 1/5th of the osmium in the oceans could be derived via interaction of MORB with seawater within hydrothermal systems [1].

That seawater reacting with hot oceanic crust mobilizes osmium has been shown by the osmium isotopic studies of metalliferous deposits precipitated from hydrothermal fluids [4,5]. Sulfides and iron–manganese crust samples from seafloor and drill cores are enriched in Os and with $^{187}Os/^{188}Os$ ratios intermediate between that of seawater and MORB. To obtain greater insight into the hydrothermal systems we must consider the following key issues: (1) what is the osmium concentration of high-temperature fluids emanating near the mid-ocean ridge axes?; (2) what is the osmium concentration of low-temperature fluids flowing out at the ridge flanks?; and (3) to what extent is osmium from the hydrothermal fluids released into solution and mixed with the oceans? A related issue is that of the variations in osmium concentration in phase-separated fluids containing variable amounts of chlorine. We have determined the osmium isotopic composition and concentration of the high-temperature ridge-crest fluids displaying a range of chlorine contents and examined a low-temperature ridge-flank fluid as well as a sample of ambient seawater close to an active hydrothermal vent field. Initial reports of this work were presented in [6,7].

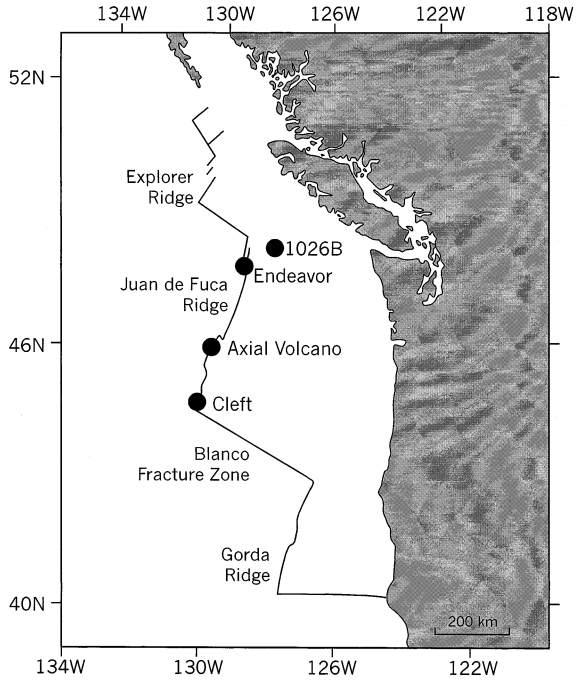

Fig. 1. Location map of the Juan de Fuca Ridge and hydrothermal vent areas.

2. Samples and analytical methods

The Juan de Fuca Ridge (JdFR) is an intermediate spreading (half spreading rate = 29 mm a^{-1}), volcanic ridge (Fig. 1). The ridge axis is free of sediment, except at the extreme northern end (north of 48°15′N), where turbidite flows cover the ridge axis to depths as shallow as 2400 m. Hydrothermal activity has been investigated at many sites including the sediment-covered middle valley, and volcanic-hosted sites at the Endeavour Segment, Axial Volcano, Coaxial Segment, and Cleft Segment. Unfiltered fluid samples with low Mg contents were selected from the three major vent fields (Fig. 1, Table 1). Fluids were collected with the *DSV Alvin* in 750 ml titanium syringe 'major' samplers [8]. Samples were transferred at sea, within 12 h of collection on the seafloor, to

Table 1
Os isotopes in hydrothermal solutions from the Juan de Fuca Ridge and the Pacific seawater

	Temperature (°C)	Mg (mmol/kg)	Cl[a] (mmol/kg)	[^{188}Os][b] (femtomol/kg)	Os[b] (femtomol/kg)	(^{187}Os/^{188}Os)$^{c}_{m}$	(^{187}Os/^{188}Os)$^{b}_{c}$
Main Endeavour							
Bastille, 1991	376	3.30	173 (148)	4.5 ± 0.1	34 ± 1	0.179 ± 0.002	0.172 ± 0.003
S and M, 1991	367	0.75	354 (351)	8.6 ± 0.3	65 ± 2	0.148 ± 0.004	0.141 ± 0.004
Grotto, 1991	355	0.57	421 (420)	8.3 ± 0.3	63 ± 2	0.135 ± 0.004	0.129 ± 0.004
Axial Volcano							
Inferno, 1998	329	1.65	351 (345)	4.1 ± 0.1	31 ± 1	0.167 ± 0.002	0.158 ± 0.002
Cleft Segment							
Monolith, 1991	308	2.38	875 (891)	25.9 ± 0.5	202 ± 4	0.387 ± 0.001	0.388 ± 0.002
Monolith, 1994	270	2.36	800 (812)	7.3 ± 0.3	55 ± 2	0.137 ± 0.001	0.130 ± 0.001
Pipe Organ, 1991	265	11.5	1086 (1237)	1.9 ± 0.1	15 ± 1	0.380 ± 0.009	0.401 ± 0.03
Low-temperature fluid							
(ODP 1026B)	50	2.42	555 (556)	69 ± 1	518 ± 10	0.111 ± 0.001	0.110 ± 0.001
Seawater around Axial Volcano							
(depth = 1764 m)		53	542	6.5 ± 0.1	55 ± 1	0.925 ± 0.009	1.01 ± 0.01
Central Pacific seawater		53	542	6.4 ± 0.1	53 ± 1	0.993 ± 0.020	1.06 ± 0.02

[a]Measured chlorine concentration. The numbers in the parentheses give the inferred values of chlorine contents after subtracting for the seawater contamination assuming that the hydrothermal fluids containing no Mg were contaminated during sampling by fresh seawater with 53 mmol/kg of Mg.

[b]Corrected for the procedural blank of 0.013 ± 0.006 fmol of ^{188}Os with ^{187}Os/^{188}Os of 0.27 ± 0.14, except for the seawater samples that were corrected using a blank of 0.037 ± 0.011 fmol of ^{188}Os with ^{187}Os/^{188}Os of 0.27 ± 0.14.

[c]Measured ratio corrected for isotope fractionation and for tracer contributions to the mixture. The power law was used for mass fractionation correction, assuming that the mass fractionation entails the OsO_3^- molecular ion. The data are normalized for mass-dependent isotope fractionation by assuming the arbitrary reference value ^{192}Os/^{188}Os = 3.08267. For reduction of the Os oxide data, the following oxygen isotopic composition was used: ^{17}O/^{16}O = 0.00037 and ^{18}O/^{16}O = 0.002047. Isotopic composition of the Os normal used for data reduction: ^{186}Os/^{188}Os = 0.11973, ^{187}Os/^{188}Os = 0.10677, ^{189}Os/^{188}Os = 1.21969, ^{190}Os/^{188}Os = 1.98146, and ^{192}Os/^{188}Os = 3.08267.

acid-cleaned high-density polyethylene (HDPE) bottles. Trace metal aliquots used for Os analysis were acidified with ultrapure ('Ultrex') HCl (2 ml per l of sample). The Endeavour samples were stored without acidification for about 7 yr in clean HDPE bottles. These samples had precipitated Fe-oxy-hydroxides and sulfides. Prior to analyses these samples were treated with pure HCl at room temperature until all the precipitates had disappeared. It is assumed the HCl treatment of the samples released into solution any Os associated with precipitates.

We analyzed samples representing a range of exit temperatures (265–376°C) and chlorine concentrations (148–1237 mmol kg^{-1}) (Table 1). Additionally, a sample of low- temperature, off-axis fluid (60°C) was analyzed. This sample was from ODP hole 1026B (Leg 168) drilled on 3.5 million yr old oceanic crust on the eastern flank of JdFR [9]. Low-temperature fluid began flowing out of the hole within 2 weeks of penetrating basaltic basement and continued to seep out after installation of a CORK [9]. Two years after drilling, sample 1026B was extracted from fluids flowing through a steel pipe and not venting directly into the ocean. Our sample was taken with a titanium major sampler, acidified with pure HCl and stored in a clean HDPE bottle. This sample is similar to the warm springs (26°C) discovered recently in this area [10]. Further details about this sample can be found in [11].

We analyzed a sample of ambient seawater from a depth of 1764 m about 13 km west–northwest of the Axial Volcano (46° 03.18 N, 130° 09.55 W). This seawater sample was collected using a Niskin sampling apparatus and stored unfiltered and un-acidified in a trace element clean collapsible HDPE bottle. Sharma et al. [1] had

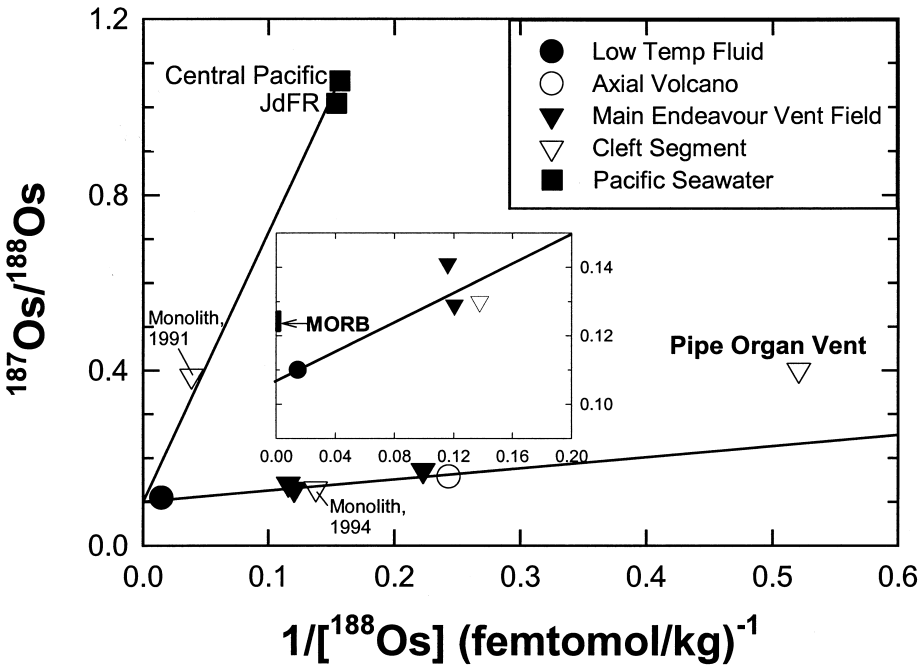

Fig. 2. Inverse of ^{188}Os versus $^{187}Os/^{188}Os$ diagram showing that one sample (Monolith, 1991) plots on the mixing line between seawater and a component with $^{187}Os/^{188}Os = 0.11$. All other samples define a nearly horizontal array that can be attributed to nearly quantitative precipitation of Os during the ascent and cooling of the hydrothermal fluids.

reported the osmium isotopic composition of an aliquot of this sample and had inferred a 20% decrease in the measured $^{187}Os/^{188}Os$ towards the MORB end-member. The data, however, were not accurate because of the uncertainty in the ratio of chemical yield to blank. The samples reported here were analyzed for Os using a recently established technique that is much more reliable than that employed before (see below). In addition, a sample of seawater collected from a depth of 2000 m in the Central Pacific (22° 45 N, 158°W) was also examined. This sample was obtained in a pre-cleaned Niskin apparatus. The sample was not filtered. It was acidified immediately after collection to 0.024 M using ultrapure HCl and stored in a pre-cleaned HDPE bottle.

Mg was analyzed on shore either by ICP-AES (2-σ rsd 2%) or by ion chromatography (2-σ rsd 1%). Chloride was analyzed by titration using $AgNO_3$ with visual endpoint (2-σ rsd 0.5%). Additional details on sampling and analytical methods can be found in [12,13]. The methods for Os analysis are described in [14].

2.1. Os blanks

Samples were divided in two sets (Set-I = all hydrothermal fluids, Set-II = seawater samples). Two procedural blanks were determined along with each set of the samples using 30 to 50 g of pure water and following the complete procedure in [14]. It was found that in comparison to the Set-I, the blanks for the Set-II had increased by a factor of 3. The total ^{188}Os blank of this procedure for Set-I of samples was 0.013 ± 0.006 fmol with $^{187}Os/^{188}Os = 0.27 \pm 0.14$ ($N = 2$). Total ^{188}Os blank for the Set-II was 0.037 ± 0.011 fmol ($N = 2$). The $^{187}Os/^{188}Os$ ratio during Set-II was not measured and was assumed the same as for Set-I. The reason for the observed increase in the blanks is not clear. As the blanks from the two sets were sharply different, they were not combined. Instead, the samples from each set were blank corrected using the values obtained in that set. The blank correction in all cases is 5% or less for the isotopic composition and 10% or less for concentration (except for the Pipe Organ sample

where blank correction is 18% for concentration; see Table 1). While we believe that any Os contamination in the laboratory procedures is well controlled and monitored, the question of contamination during sample collection remains an issue that can only be addressed with more extensive and replicate sampling procedures.

3. Results and interpretation

Table 1 gives the osmium concentrations (C_{Os}) and $^{187}Os/^{188}Os$ ratios, both measured and corrected for blank. The C_{Os} of the high-temperature hydrothermal fluids range from 15 to 202 fmol kg^{-1}. The $^{187}Os/^{188}Os$ corrected for blank vary from 0.129 to 0.388. In contrast, C_{Os} of the low-temperature ridge-flank fluid is 518 fmol kg^{-1}. Most remarkably, this sample has $^{187}Os/^{188}Os = 0.110 \pm 0.001$, much less than MORB ($\sim 0.125$), indicating the presence of an ancient depleted domain under the JdFR [7] (see below). We note that two samples (Monolith, 1991 and the low-temperature fluid) have highly elevated Os concentrations. It is conceivable that sampling procedures could be responsible for contamination by non-radiogenic Os. However, there is no evidence of significant contamination in any of the other samples. We will, therefore, assume that the data truly represent the fluids sampled. The sample of Central Pacific seawater gives $C_{Os} = 53 \pm 1$ fmol kg^{-1} and $^{187}Os/^{188}Os$ ratio $= 1.06 \pm 0.02$. The isotopic composition of the Central Pacific sample is identical to that estimated for another sample from this area [1]. However, the C_{Os} is about a factor of 3 higher than that reported previously by us and is in excellent agreement with the concentration reported in [3] for the Indian Ocean using an improved procedure. The sample of seawater around the Axial Volcano gives $C_{Os} = 55 \pm 1$ fmol kg^{-1} and $^{187}Os/^{188}Os$ ratio $= 1.01 \pm 0.02$. While the C_{Os} of this sample is nearly the same as the Central Pacific seawater, the $^{187}Os/^{188}Os$ ratio is lower by $\sim 4\%$ over seawater (Table 1). As both the samples have been blank corrected using Set-II blanks (Table 1), we believe that the difference between the two isotopic ratios is real. However, this difference is just at the margin of possible errors.

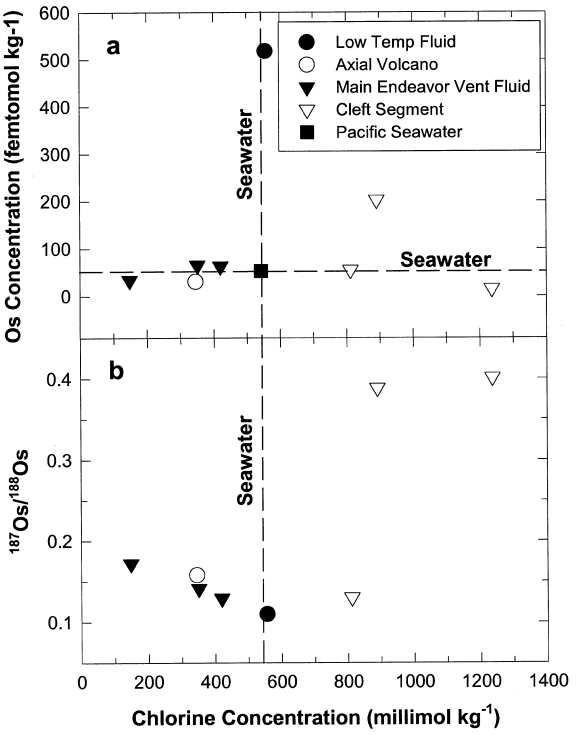

Fig. 3. Variation of osmium concentration (a) and isotopic composition (b) with chlorine contents. Phase-separated fluids do not appear to have dissimilar proportions of Os, indicating buffering by some other reaction that followed phase separation.

The behavior of Os in the hydrothermal fluids can be seen from inspection of Fig. 2, where we plot $^{187}Os/^{188}Os$ versus $1/C_{Os}^{188}$. Here the conservative mixing of two end-members would produce mixtures that lie on a line connecting the endpoints. If C_{Os} of the hydrothermal fluids were buffered, then the line would extend vertically from the seawater endpoint to the isotopic composition of MORB. Three samples lie close to this endpoint. If the hydrothermal fluids had very high C_{Os} compared with seawater, then the line would connect with the MORB end-member near $1/C_{Os} \sim 0$. Two samples lie on such a trajectory. However, another set of data lies close to a line which would correspond to mixtures of hydrothermal fluids of high Os concentration with an end-member with $C_{Os} < 15$ fmol kg^{-1} and

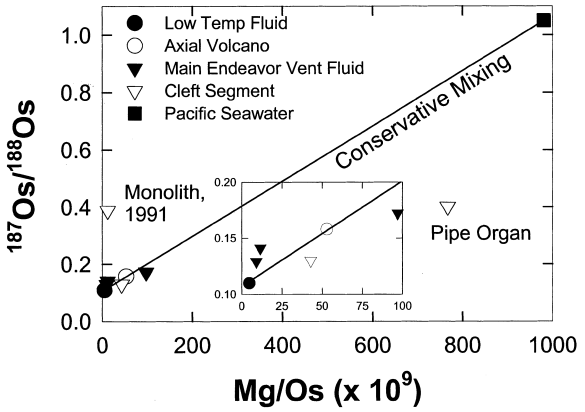

Fig. 4. Mg/Os versus $^{187}Os/^{188}Os$ diagram to evaluate the role of seawater mixing in influencing the Os isotopic composition of the Mg depleted hydrothermal fluids. The solid line is a conservative mixing line between a hydrothermal component (Mg/Os = 0, $^{187}Os/^{188}Os = 0.125$) and seawater (Mg/Os = 964×10^9, $^{187}Os/^{188}Os = 1.06$). All samples, except one from Axial Volcano, do not fall along the conservative mixing line (see also the insert) indicating that the seawater mixing is not conservative.

$^{187}Os/^{188}Os = 0.2–0.3$. It is evident that Os behavior in these systems is complex and non-conservative.

The mechanism controlling the solubility of Os in hydrothermal fluids is not known. If chloride complexes are a dominant control then some correlation with Cl concentration is expected. Fig. 3a shows that this is not the case. Six of the eight samples have concentrations close to that of seawater over a wide range of Cl concentrations. This apparent constancy in concentration appears to support a model of some kind of buffering. From samples of high Cl fluids, the same vent (Monolith) gives widely varying Os concentrations ranging from near seawater concentration to $\sim \times 4$ higher. The low-temperature fluid with seawater chlorinity is enriched in Os concentration by a factor of 9. The $^{187}Os/^{188}Os$ ratio is essentially independent of chlorinities below 800 mmol kg^{-1} but two high-chlorinity samples have much higher values, yet far below that of seawater (Fig. 3b).

To examine the hydrothermal end-members and how the samples are affected by entrainment of seawater, we plot $^{187}Os/^{188}Os$ versus Mg/Os (Fig. 4). This plot is linear during *conservative* mixing of hydrothermal end-members with seawater. Assuming that we start with an Mg-free hydrothermal fluid in the upflow zone, Mg can be added at the point of sampling by entraining ambient seawater, or below the seafloor if seawater enters the upflow conduit. Fig. 4 and its insert show that most of the fluids do not fall on a conservative mixing line, indicating that mixing of seawater with Mg-free hydrothermal fluids is complex and non-conservative.

4. Discussion

We now address the problem of Os transport considering current views on hydrothermal systems. It is clear that mechanisms must exist for providing hydrothermal fluids with high Os concentrations, with concentrations close to seawater, and for the mixing of seawater with high $^{187}Os/^{188}Os$ with 'pure' hydrothermal solutions that are close to MORB sources in isotopic composition. There is also the issue of the nature of diverse isotopic sources suggested by the data on the low-temperature fluid.

4.1. Sources and transport of Os in hydrothermal fluids

The platinum group elements including Os are distributed in MORBs in trace iron–, copper–, nickel–sulfide phases (abundance = 3 to 70 μg g^{-1}) [15] that generally reside in spherules or on inter-granular boundaries. These phases are greatly enriched in Os relative to the whole rock and contain about 90% of this element in MORBs [15]. As a result, the degree of alteration necessary to extract the Os by decomposition of sulfide phases needs not be as extensive as that necessary to extract other elements that are distributed through major and minor minerals, unless there are strong controls on the solubility of Os. For a water/rock ratio of 1–2 that is typically determined for other soluble elements in many hydrothermal fluids, this would correspond to C_{Os} of 1300 to 2600 fmol kg^{-1}, assuming the bulk rock contained 2600 fmol kg^{-1} Os ($\sim$0.5 pg/g) and that all Os is soluble.

From the arguments given above, it is evident that very high concentrations can be readily provided by dissolution of sulfide phases in basalts. There are clearly hydrothermal solutions with high Os concentration and purely mantle $^{187}Os/^{188}Os$ ratios (e.g. the low-temperature fluid, LTF). We consider that the mantle value of $^{187}Os/^{188}Os$ of the source cannot be significantly lower than ~0.110. A comparison between the $^{187}Os/^{188}Os$ ratios of seawater and the LTF therefore requires that the concentration in the original fluid had to be over ~1000 times that in seawater, if we assume that it results from a single stage of dissolution without precipitation. However, the high-temperature hydrothermal fluids with very low Mg are not extremely enriched in Os, pointing to its scavenging during the transport of the fluids from the reaction zone to the seafloor. There are also many samples that exhibit somewhat elevated to greatly elevated $^{187}Os/^{188}Os$ ratios relative to MORB. This requires mixing of the hydrothermal fluids with a source of radiogenic Os, the obvious source being seawater.

With regard to removal of Os as the fluid moves toward the seafloor, there is evidence of abundant precipitation of sulfides (mainly pyrite), anhydrite, and silica [16]. Presumably it is in such precipitation processes that Os is removed by some carrier phases. In analogy with magmatic sulfides pyrite appears to be the most promising scavenger among the above minerals. However, pyrite precipitated at low pH but in the presence of large amounts of dissolved iron is positively charged [17] and may not scavenge Os efficiently which is preferentially absorbed onto negatively charged phases [18]. Indeed, in comparison to the magmatic sulfides (C_{Os} = 250–2500 × 10^6 fmol kg^{-1}) [15], the C_{Os} of TAG sulfides precipitated at a depth of 80 m below seafloor is only 200–400 fmol kg^{-1} [4]. As pyrite is a ubiquitous mineral in veins and massive sulfides [16], this suggests that it may possibly control C_{Os} of the hydrothermal fluids prior to their injection into the sea.

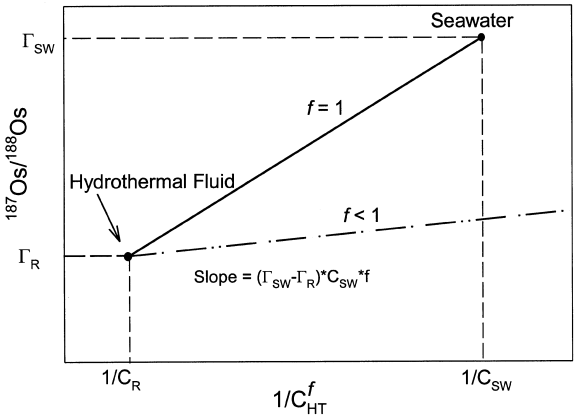

Fig. 5. Mixing of seawater Os with rock-derived Os will lead to the formation of hydrothermal fluids whose Os isotopic composition will be weighted by the relative number of Os atoms contributed by the seawater and the rock. If such a fluid then looses a fraction $(1-f)$ by precipitation during ascent, the resulting concentration (C^f_{HT}) will be related by $\Gamma_{mix} = \Gamma_R + (\Gamma_{SW} - \Gamma_R) f C_{SW}/C^f_{HT}$ (see text). The apparent endpoint of this line is at $(1/fC_{SW}, \Gamma_{SW})$.

Osmium removal via precipitation may take place as hydrothermal fluids from a hot reaction zone thus formed move upward through the discharge zone and cool conductively and/or by mixing with seawater. As the Os in hydrothermal fluids is a result of water–rock interaction, we are led to consider a simple single stage model of extraction of Os from the rock into the seawater during hydrothermal circulation. The net high-temperature fluid that will appear at the seawater interface is the reaction-zone fluid modified by precipitation and mixing with crustal seawater. The concentration of an isotope in a hydrothermal solution resulting from the extraction of an element from a mass of rock (M_R) in a volume of what was originally seawater is:

$$C_{HT} = \frac{C_R M_R + C_{SW} M_{SW}}{M_{SW}} \quad (1)$$

where C is the concentration of the isotope in R or SW, M_R is the mass of reacting rock and M_{SW} is the mass of seawater. The isotope ratio (Γ) of this mixed fluid is:

$$\Gamma_{mix} = \frac{\Gamma_R C_R M_R + \Gamma_{SW} C_{SW} M_{SW}}{C_R M_R + C_{SW} M_{SW}} \quad (2)$$

If a fraction $(1-f)$ of this mixture is precipitated, the resulting concentration is diminished

by a factor f but the isotopic composition is unchanged. The resulting concentration is $fC_{HT} \equiv C^f_{HT}$. The resulting equation governing Γ_{mix} is thus:

$$\Gamma_{mix} = \Gamma_R + (\Gamma_{SW} - \Gamma_R) f C_{SW} / C^f_{HT} \quad (3)$$

Eq. 3 describes a straight line in a Γ_{mix} versus $1/C^f_{HT}$ passing through Γ_R for $C^f_{HT} \rightarrow \infty$ and a slope of $(\Gamma_{SW} - \Gamma_R) f C_{SW}$. A schematic diagram is given in Fig. 5. If this fluid were to mix later with some seawater upon injection into the ocean, a similar calculation could be repeated. This would describe a different trend, but would presumably be suggested by the presence of Mg. If there is Os fractionation during two-phase separation, then the relationships are more complicated. For a fluid that has not undergone this separation, the Cl content should be that of seawater. In Fig. 2, if we take the trend with low slope (=0.217), this corresponds to $f = 0.036$. The steep trend corresponds to $f = 1.0$. It appears that the two extreme trends defined by the data are: (1) one where there has been predominant precipitation of Os prior to entry of the hydrothermal fluid into the ocean, and (2) one where there has been very little precipitation. We note that from Eq. 3, when $C^f_{HT} \approx C_{SW}$ then $C_{HT} \approx C_{SW}/f$. For $f = 0.036$ this gives $C_{HT} = 1500$ fmol kg^{-1}, which is just what we think the fluids should have been like without precipitation. We note that an insightful presentation of hydrothermal alteration processes for the basal seawater system that includes continuous reaction, exchange and continuous precipitation has been given by [19]. It is very possible that the actual reaction path involves continuous exchange between basaltic and hydrothermal fluid Os and concurrent precipitation. However, considering our lack of knowledge of Os chemistry and the phases involved, we have treated the problem in a simpler manner as a single-stage process.

We now seek to use the isotopic composition and concentrations of ^{188}Os as related to the Mg concentrations with the hope of gaining some insight into aspects of the transport processes. We note that if the addition of seawater to a hydrothermal fluid in shallow or near surface conditions was conservative, then the concentration of ^{188}Os should be calculated (C^{CALC}_{Os}) by an isotope dilution equation using the Mg content as a measure of the seawater fraction. This may be compared with the measured ^{188}Os concentration. If there is precipitation of Os after mixing, then the calculated concentration will be greater than the measured value. The resulting equation is:

$$C^{CALC}_{Os} = \frac{C^{mix}_{Mg}}{C^{SW}_{Mg}} \times C^{SW}_{Os} \times \left(\frac{\Gamma_{SW} - \Gamma_{HT}}{\Gamma_{mix} - \Gamma_{HT}} \right) \quad (4)$$

where Γ_{HT} is the ^{187}Os/^{188}Os ratio of the hydrothermal fluid prior to mixing. The minimum value of C^{CALC}_{Os} is obtained for the minimum value of Γ_{HT}. If we take $\Gamma_{HT} = 0.110$, then it can be seen that the Pipe Organ, which has a high Mg content, should have 4.9 fmol kg^{-1}, while the measured value is 1.9 fmol kg^{-1} indicating that it has been depleted by a factor of 2.5 after seawater mixing. If the actual hydrothermal fluid had a higher value than $\Gamma_{HT} > 0.110$, then the losses would have been greater. In contrast, many of the other samples yield C^{CALC}_{Os} less than the measured values. In particular, the sample Monolith, 1991 gives a calculated value far below that which was measured. This indicates that the Γ_{HT} in these samples just prior to mixing must in fact be far above the value $\Gamma_{HT} = 0.110$ and be close to the measured values. We infer that the hydrothermal fluids thus have been evolved with widely varying Γ values during the flow of the hydrothermal fluid within the basalts. This means that widely varying R/W ratios are responsible for the range from very low Γ values to those almost halfway to that of SW. This must reflect flow paths and degrees of depletion of Os in the source basalts with the passage of water masses. We thus see that Os precipitation in the hydrothermal fluids is a dominating process prior to encountering the seawater interface. A possible basis for explaining the lack of extreme depletion in Os in the LTF compared with other samples may be that fluids at high temperature have much larger amounts of other elements (compared to LTF fluids) which precipitate out on ascent, thus providing a more effective scavenging mechanism for Os and other elements. The low-temperature fluids circulating in

basaltic basement have no measurable sulfide, hence no capacity to scavenge Os by pyrite precipitation.

4.2. Hydrothermal versus cosmic inputs of Os into the oceans

In this section, we first estimate the extent to which the unradiogenic Os component of seawater is derived from hydrothermal sources by neglecting the cosmic dust input. Utilizing the new seawater concentration data, we then evaluate the contribution of unradiogenic Os through the dissolution of cosmic dust.

We apply the steady state solution for Os in seawater (SW) with two different isotopic sources comprising rivers (C) and hydrothermal sources (H), neglecting the cosmic dust contribution. For simplicity, we will assume that the input represents that of 'pure' values to be associated with the upper mantle (H) and crust (C). If, however, the hydrothermal $^{187}Os/^{188}Os$ ratios were due to blending of a mantle source and seawater, then the calculations would be shifted with the flows increased. We have:

$$\Gamma_{Os}^{SW} = X_{Os}^{C}\Gamma_{Os}^{C} + (1-X_{Os}^{C})\Gamma_{Os}^{H} \quad (5)$$

where Γ^{i} represents ($^{187}Os/^{188}Os$); $X_{Os}^{C} = 1/[1 + (J_{^{188}Os}^{H}/J_{^{188}Os}^{C})$ is the fraction of Os from rivers, and $J_{^{188}Os}^{j}$ represents flow of ^{188}Os from j = C, H. The ratio of hydrothermal flow rate to the river flow rate (R_{Os}) can be obtained from:

$$R_{Os} \equiv \frac{\Gamma_{Os}^{C} - \Gamma_{Os}^{SW}}{\Gamma_{Os}^{SW} - \Gamma_{Os}^{H}} = \frac{J_{^{188}Os}^{H}}{J_{^{188}Os}^{C}} \quad (6)$$

The J^{H}/J^{C} is also given by the relation:

$$\frac{J^{H}}{J^{C}} = \frac{\dot{W}^{H} C_{Os}^{H}}{\dot{W}^{C} C_{Os}^{C}} \quad (7)$$

where $\dot{W}^{j}$ = mass flow rate of water, and C_{Os}^{j} is the concentration of Os in water from j. We will assume that the dissolved Os load in rivers is carried into the deep sea and is not lost in estuaries [20].

4.2.1. Assessment of $\dot{W}^{H}$ using Sr isotopes

An equation identical to Eq. 5 can be written for seawater Sr assuming that the diagenetic contribution is negligible. From the values given in Table 2, we obtain $R_{Sr} \approx 0.46$ so that $J_{^{86}Sr}^{H}/J_{^{86}Sr}^{C} = \dot{W}^{H} C_{Sr}^{H}/\dot{W}^{C} C_{Sr}^{C} \approx 0.46$. As Sr appears to be buffered in high-temperature hydrothermal fluids [21–23] we have $C_{Sr}^{H} \approx C_{Sr}^{SW}$ so that $\dot{W}^{H} C_{Sr}^{SW}/\dot{W}^{C} C_{Sr}^{C} = 0.46$. Using the average values in Table 2 we find $\dot{W}^{H} = 1.7 \times 10^{14}$ kg/yr which is similar to that previously estimated by other workers [22,24,25]. Note that in our calculation, it is not evident whether the $\dot{W}^{H}$ represents just the high-temperature transport or is close to the total water transport (see also [21–23]).

4.2.2. R_{Os} comparisons

From the values given in Table 2 and using Eq.

Table 2
Parameters used in the text

Parameter	Symbol	Value
Present seawater $^{187}Os/^{188}Os$	Γ_{Os}^{SW}	1.06
Continental $^{187}Os/^{188}Os$	Γ_{Os}^{C}	1.26
Juan de Fuca hydrothermal $^{187}Os/^{188}Os$	Γ_{Os}^{H}	0.110
Total number of Os atoms in seawater	N_{Os}^{SW}	74×10^{6} moles
Mean residence time of Os in the oceans	τ_{Os}	40 ka
River water flow	$\dot{W}^{C}$	3.74×10^{16} kg a^{-1}
Concentration of Os in i (i = C or SW)	C_{Os}^{i}	$C_{Os}^{SW} = 55 \times 10^{-15}$ mol kg^{-1} $C_{Os}^{C} = 50 \times 10^{-15}$ mol kg^{-1}
Present seawater $^{87}Sr/^{86}Sr$	Γ_{Sr}^{SW}	0.7091
Continental $^{87}Sr/^{86}Sr$	Γ_{Srs}^{C}	0.7119
Hydrothermal $^{87}Sr/^{86}Sr$	Γ_{Os}^{H}	0.7030

6 we obtain: $R_{Os} = 0.2$. We note that the value of R_{Os} determined this way depends only on the isotopic composition of seawater, hydrothermal input and continental input. Γ^{C}_{Os} is assumed here to be equal to the average eroding upper continental crust [2]. If the Γ^{C}_{Os} delivered by the rivers is much higher than that of the average eroding upper continental crust [26] it will lead to an increase in R_{Os}. However, direct measurements of isotopic composition of rivers suggest that the riverine $^{187}Os/^{188}Os$ is similar to the upper continental crust [14,27].

Using Eq. 7 and data in Table 2 and assuming that C^{H}_{Os} for the high-temperature fluids is buffered (i.e. $C^{H}_{Os} \approx C^{SW}_{Os}$), we find $J^{H}/J^{C} = 5.7 \times 10^{-3}$. This value is about 35 times less than that calculated using the isotopic arguments ($R_{Os} = 0.2$, Eq. 6) and shows that when the Os contribution is buffered (e.g. the high-temperature ridge-crest fluids), the contribution is negligible for this flow rate. This indicates that the unradiogenic Os contribution to the oceans must be derived from either hydrothermal fluids when they are not buffered (e.g. low-temperature alteration), from much larger flow rates ($\dot{W}^{H}$) or from the dissolution of cosmic dust.

Using data from low-temperature mineral precipitates, it has been suggested that low-temperature fluids may be significant contributors to the seawater unradiogenic Os budget [5]. From heat flow arguments, low-temperature (5 to 15°C) alteration of basalt may involve water flows of the order of 100 to 300 times those estimated for the ridge-crest hydrothermal fluids [22]. Assuming that the average C_{Os} of the low-temperature liquids is buffered ($C^{H}_{Os} \approx C^{SW}_{Os}$), and rate of water flow 100 to 300 times the value of $\dot{W}^{H}$ obtained for Sr, we find that $J^{H}/J^{C} = 0.45$ to 1.36, which is much higher than $R_{Os} = 0.2$ calculated using the isotopic arguments. This indicates that the Os contributions from the low-temperature liquids even when buffered are more than sufficient to provide all the unradiogenic Os component. The one low-temperature fluid that has been studied has a factor of 9 higher Os concentration than that of seawater. If this were typical of low-temperature fluids, it would require that most of the Os be precipitated prior to mixing with seawater, otherwise there would be a gross oversupply. There is thus an ample source of Os in low-temperature fluids if the sample analyzed here is representative. A detailed balance is difficult to make because of the number of variables, including the effective value of $^{187}Os/^{188}Os$ that is transported from the bulk hydrothermal system.

4.2.3. Cosmic dust contributions

Using the new seawater C_{Os} data ([3]; this study), we can revise our estimates of the bound on net mass infall rate of cosmic dust [1]. Assuming that Os in deep-sea marine sediments (Sed) is derived from cosmic dust (CD) and seawater, the cosmic dust infall rate (J_{CD}) into the oceans is given by:

$$J_{CD} = \left(\frac{\Gamma^{Sed}_{Os} - \Gamma^{SW}_{Os}}{\Gamma^{CD}_{Os} - \Gamma^{Sed}_{Os}} \right) \times \frac{N^{SW}_{Os}}{\bar{\tau}_{Os}} \quad (8)$$

where N^{SW}_{Os} is the number of Os atoms in seawater and $\bar{\tau}_{Os}$ is the mean residence time of Os in the oceans. The $^{187}Os/^{188}Os$ of recently deposited deep-sea clay from the Domes Site C is 0.79 ± 0.2 [28]. Using the parameters in Table 2, this gives a $J_{CD} = 4.2 \times 10^{-14}$ g Os cm^{-2} a^{-1}. Assuming chondritic Os abundance for the dust (= 490 ng/g), we find the mass flux of cosmic dust = 8.6×10^{-8} g cm^{-2} a^{-1} or a mass infall rate on the Earth of 4.4×10^{11} g a^{-1}. If a fraction f_e of incoming dust is evaporated and contributes to the unradiogenic Os dissolved in seawater, the infall would contribute $\sim$295 mol a^{-1} of Os to the oceans using $f_e = 0.26$ (see [1]), nearly sufficient to account for the low $^{187}Os/^{186}Os$ component in seawater. This calculation suggests that there is still a problem with balancing of the relative contributions of hydrothermal fluids and evaporated cosmic dust. The above calculation is subject to errors if the measured $^{187}Os/^{188}Os$ of the bulk sediments is affected by sedimentary redistribution of cosmic dust. If the analyzed bulk sediments deposited per unit time contain a larger portion of cosmic dust per unit mass due to sedimentary refocusing, it would lead to a lower measured $^{187}Os/^{188}Os$ ratio and an increase in J_{CD}. That cosmic dust refocusing takes place is evident from other deep-sea sediment cores where

the abundances of cosmic dust-derived ^{3}He and seawater produced ^{230}Th are positively correlated (e.g. [29]). The extent to which the measured $^{187}Os/^{188}Os$ in the clays from Domes Site is affected by sedimentary processes is not clear at present. The estimated cosmic dust infall given here is about 10 times greater than that estimated by Love and Brownlee [30] but it is within the range of values estimated by other workers (cf. summary by [31]). From the above discussion it is evident that either the low-temperature hydrothermal alteration or dissolution of cosmic dust can provide the unradiogenic Os component dissolved in the oceans. The matter of the provenance of the unradiogenic component of seawater Os thus appears to be unresolved. If low-temperature hydrothermal sources govern the unradiogenic Os into the oceans, the estimated proportion of cosmic dust-derived Os in the seawater would be substantially reduced.

4.3. The Osmium isotopic composition of MORBs

The $^{187}Os/^{188}Os$ ratios of the hydrothermal fluids that have been measured are variable and range from 0.110 to 0.401. The interpretation is that this is due to the relative proportion of seawater Os and basaltic Os in the samples. Estimates of the $^{187}Os/^{188}Os$ of MORB source have been obtained by measurements of abyssal peridotites and one sulfide sample and range from 0.121 to 0.128 (average $^{187}Os/^{188}Os = 0.125$) [15,32]. Most leached MORBs and sulfides have more radiogenic values. We note that the low-temperature fluid (LTF) shows $^{187}Os/^{188}Os = 0.110$ that is substantially lower than these MORB values. All other fluids have $^{187}Os/^{188}Os$ ratios above MORB. We are thus faced with the question of whether the ridge-flank basement fluid from 1026B (LTF) is derived from a special source, while the others represent seawater interaction with 'normal' MORBs; or if all of the fluids at this site are modified from the value of the LTF. In either case, the low value of the LTF must be addressed.

It must first be recognized that the Re–Os system is quite distinct from the Sm–Nd, Rb–Sr or U–Th–Pb systems. There is a substantial inventory of the parent and daughter elements of these elements in the crust as well as the mantle. In contrast, for the Re–Os system, while there is a great fractionation between Re and Os in forming continental crust, the concentrations of both Re and Os are so low in crustal rocks that the inventory in the mantle is left almost unchanged. As a result, the bulk mantle isotopic evolution must follow that of a simple system with the present value very close to the chondritic ratios and should exhibit little memory of continental crustal extraction events. This would also be true for all parts of the mantle if well mixed. If, however, the mantle contains domains with time-integrated Re/Os ratios much lower or much higher than the bulk mantle, and if such domains are sampled, their $^{187}Os/^{188}Os$ ratios would be a measure of the time of the Re/Os fractionation.

The $^{187}Os/^{188}Os$ ratio of the present-day bulk mantle is ~ 0.129 [33]. For an initial $^{187}Os/^{188}Os = 0.0956$ found for the iron meteorites [34,35], the $^{187}Re/^{188}Os$ of the bulk mantle is 0.46, assuming that the Earth formed at 4.45 Ga. The LTF $^{187}Os/^{188}Os$ represents the chondritic Os isotopic ratio at about 2.6 Ga ago (= chondrite model age). The results, therefore, demonstrate that the mantle source of the Os in the LTF Os must be a relict of differentiation processes that occurred in the Archean and has been preserved.

It follows from the above conclusion that an ancient depleted mantle reservoir is/was present under JdFR. The only reservoir we know to have low $^{187}Os/^{188}Os$ is subcontinental lithosphere (e.g. [36]). It has frequently been suggested that such lithosphere can be delaminated from the subcontinental region and can thereby reenter the convective portion of the mantle (e.g. [37]). Another mantle reservoir that can potentially provide low $^{187}Os/^{188}Os$ consists of neutrally buoyant ultramafic residues of partial melting of mantle material. Evidence of the presence of such ancient ultramafic material comes from ophiolite complexes where these distinctive units are found associated with much younger lavas [38,39].

We postulate that the MORB magmas at the Juan de Fuca east flank site penetrated very ancient (at least 2.6 Ga old) depleted materials in the upper mantle and that the observed Os isotopic

signature reflects the contamination of the basaltic magma with the Os in this material. This hypothesis requires that there is at least partial equilibrium between the Os from the ancient depleted material and the cross cutting basaltic melts. The extent to which this model is generally valid can be seen from the $^{187}Os/^{188}Os$ ratios of abyssal peridotites sampled so far yield chondrite model ages of 0.2 Ga up to 1.2 Ga, indicating that the existence of ancient depleted domains within the upper mantle is more a rule than an exception. Proposals of MORB sources with very high Re/Os (e.g. pyroxenitic material) would lead to negative model ages that have not been observed.

5. Conclusions

The Os data from hydrothermal fluids of the Juan de Fuca Ridge and east flank indicate: (1) a nearly complete Os isotopic exchange between the interacting seawater and mid-ocean ridge basalt; (2) substantial subsurface enrichment of Os in the hydrothermal fluid and then strong depletion of Os in the subsurface high-temperature ridge-crest environment prior to entering the ocean; (3) extensive Os mobilization and transfer to the seafloor in warm (60°C) reaction zones.

A simple model of seawater–basalt interaction and Os release followed by its precipitation is proposed that emulates the observed isotopic composition and concentration of the hydrothermal fluids. It is inferred that while the $^{187}Os/^{188}Os$ of the hydrothermal fluids result from variable water/rock ratios, their Os concentrations are often a consequence of nearly quantitative precipitation that occurs during the ascent and cooling of the fluids. It is suggested that such a process has masked any variation in Os concentration resulting from phase separation. The proposed model for Os may also be used for examining the variations in the concentrations of any two elements with similar chemical behavior or conversely to assess which elements behave similarly in the hydrothermal environment.

Our results demonstrate that the Os concentration of the high-temperature ridge-crest fluids is typically close to the concentration of seawater and thus appears to be buffered by some chemical reaction. This implies that the Os supplied by high-temperature fluids is not sufficient to account for the observed unradiogenic Os component in the oceans. In contrast, the low-temperature off-axis fluids, when buffered, may still provide more than enough Os to account for the observed unradiogenic Os component in the oceans. Indeed, the calculations require that a large amount of Os released during low-temperature alteration be buried without mixing into the oceans.

The results also indicate that the Os isotopic composition and concentration in the Pacific and the Indian oceans are uniform. Using the new seawater concentration data, we revise our previous estimates on the upper bound to the cosmic dust infall ($=4.4\times10^{11}$ g a^{-1}). With regard to the relative contributions of Os via low-temperature seafloor alteration and cosmic dust dissolution, we demonstrate that either of these two sources is sufficient to account for all the unradiogenic Os in the oceans. A detailed balance between the low-temperature hydrothermal and cosmic contributions to the unradiogenic component is, therefore, not yet possible.

We postulate that MORBs on the east flank of the Juan de Fuca Ridge were formed from the melts that penetrated through and interacted with slabs of ancient depleted mantle. This is supported by our previous conclusions that the convecting upper mantle contains ancient depleted ultramafic material that is depleted in terms of light rare earths [39,40]. That such a material is present in the upper mantle can be unambiguously demonstrated using Os isotopes.

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